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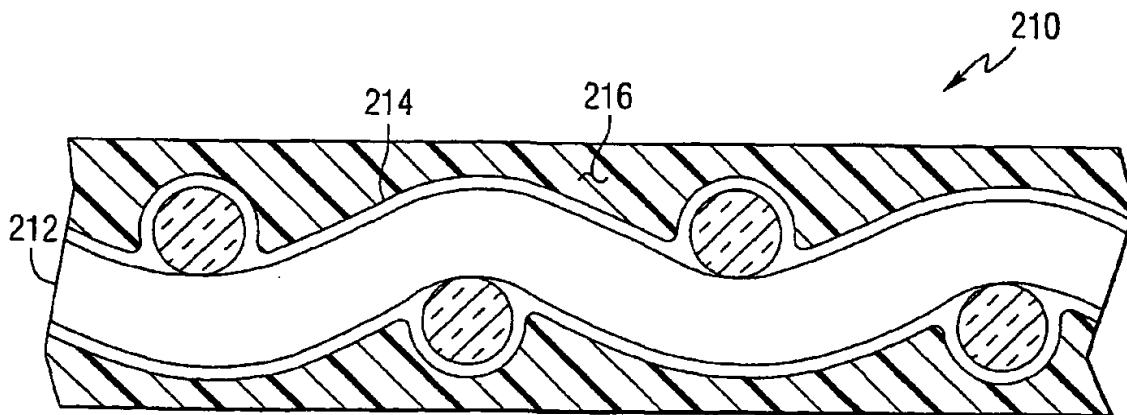
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(54) Title: RESIN COMPATIBILIZED STARCH-OIL SIZING



(57) Abstract: A method a forming a resin compatible fabric (210) includes: (A) forming a fabric with a plurality of fiber strands, wherein at least one of the plurality of fiber strands includes a plurality of fibers and at least one of the plurality of fibers includes an at least partial coating (214) having at least one starch material with at least one hydroxyl group; (B) breaking a bond between a hydrogen atom of a hydroxyl group of a first starch molecule of the at least one starch material with an oxygen atom of a second starch molecule of the at least one starch material to form at least one unreacted hydroxyl group on the first starch molecule; and (C) reacting at least one functional group of a second material with the at least one unreacted hydroxyl group of the at least one starch material to form a grafted starch material after interweaving



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## RESIN COMPATIBILIZED STARCH-OIL SIZING

### Cross Reference to Related Patent Applications

5           This application claims the benefit of U.S. Provisional Application No. 60/233,140 filed September 18, 2000.

          The present invention relates generally to sizings for fibers and fibers coated therewith and, more particularly to starch-oil sizings modified for resin compatibility  
10   and glass fibers coated therewith. The present invention further relates to glass fabrics formed from the coated glass fibers of the present invention, as well as to finishing sizes for glass fabrics.

          Glass fibers used in textile applications are generally coated or sized after forming with a sizing composition typically based on an aqueous starch-oil  
15   composition. As used herein, the terms "size" or "sizing" refer to any coating composition applied to the fibers after formation. Such starch-oil sizing compositions are well known in the art and are generally effective in imparting good processing and handling characteristics to the glass fibers coated therewith. Examples of typical starch-oil sizing compositions are given in K. Loewenstein, The Manufacturing  
20   Technology Continuous of Glass Fibres, (3d Ed. 1993) at pages 238-244, which are hereby incorporated by reference. Although such sizing compositions are effective in providing for good weavability of the glass fiber strands and yarns, when used as reinforcing materials they are typically not compatible with the resin matrix materials into which the sized fibers are commonly incorporated. For example, starch-oil sizing  
25   compositions are not compatible with epoxy resins systems used to form printed circuit boards into which woven glass fabrics comprising fibers sized with the starch-oil compositions are commonly incorporated. Accordingly, it is conventional practice in the industry to remove the non-resin compatible starch-oil sizing from the surface of the glass fibers prior to their incorporation into a matrix material by subjecting the  
30   glass fibers to elevated temperatures, e.g. heating the fabric at 380°C for 60-80 hours, and/or by scrubbing the fabric after weaving. These types of operations are typically referred to as heat-cleaning, de-oiling, or degreasing, and are hereinafter collectively referred to as "degreasing". Thereafter, the woven glass fabrics are recoated with a finishing sizing to improve the compatibility between the fabric and  
35   the matrix material into which the fabric will be incorporated. Finishing sizes typically comprise silane coupling agents and water.

Since degreasing processes can be both damaging to the fabric and costly, it is desirable to eliminate the need for removal of the sizing composition before incorporation into the matrix material. One method of eliminating the need for degreasing is to formulate a sizing composition that is resin compatible. As used  
5 herein, the terms "resin compatible" or "compatible with a matrix material" mean the coating composition applied to the fibers is compatible with the matrix material into which the fibers will be incorporated such that the coating composition (or selected coating components) achieves at least one of the following properties: does not require removal prior to incorporation into the matrix material (such as by  
10 degreasing), facilitates good penetration of the matrix material through the individual bundles of fibers in a mat or fabric incorporating the yarn and good penetration of the matrix material through the mat or fabric during conventional processing, and results in final products having desired physical properties and hydrolytic stability. However, while such sizing compositions can be effective in eliminating degreasing processes, and in particular heat cleaning processes, they can require significant re-formulation  
15 of the conventional starch-oil sizings.

Accordingly, it would be advantageous to develop a method of sizing glass fibers with a coating composition based upon conventional starch-oil systems and processing the coated fibers so that the sizing composition is compatible with various  
20 matrix materials, and in particular with epoxy resin systems into which the sized glass fibers are incorporated.

The present invention provides a method a forming a resin compatible fabric comprising: (A) forming a fabric comprising a plurality of fiber strands, wherein at least one of the plurality of fiber strands comprises a plurality of fibers and at least  
25 one of the plurality of fibers comprises an at least partial coating comprising at least one starch material comprising at least one hydroxyl group; (B) breaking a bond between a hydrogen atom of a hydroxyl group of a first starch molecule of the at least one starch material with an oxygen atom of a second starch molecule of the at least one starch material to form at least one unreacted hydroxyl group on the first starch  
30 molecule; and (C) reacting at least one functional group of a second material with the at least one unreacted hydroxyl group of the at least one starch material to form a grafted starch material after interweaving. In one nonlimiting embodiment, the fabric is a woven glass fiber fabric, with the glass fibers selected from E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, A-glass fibers and E-glass derivative  
35 fibers. In another nonlimiting embodiment, the function group is selected from isocyanatosilanes, methyl isocyanate, n-butyl isocyanate, cyclohexyl isocyanate, octadecyl isocyanate, phenyl isocyanate, chlorophenyl isocyanate, isopropyl

isocyanate, propyl isocyanate, dichlorophenyl isocyanate, fatty acid ester isocyanates, aliphatic isocyanates, acetic anhydride, maleic anhydride, succinic anhydride, formic acid, acetic acid, propionic acid, glutaric acid and butyric acid and high molecular weight acids selected from palmitic acid, lauric acid, stearic acid, vinyl acetate, vinyl butyrate, benzoyl chloride and cinnamoyl chloride. In one nonlimiting embodiment of the present invention, the coating further comprises the second material comprising the at least one functional group, while in another nonlimiting embodiment, a finishing size is applied to at least a portion of the fabric, the finishing sizing comprising the second material comprising the at least one functional group.

The present invention also provides for preregs, laminates and printed circuit boards incorporating the resin compatible fabric.

The present invention also provides a method of forming a resin compatible woven glass fiber fabric, comprising: (A) interweaving a plurality of glass fiber strands to form a fabric, wherein at least one of the plurality of glass fiber strands comprises a plurality of glass fibers and at least one of the plurality of glass fibers comprises an at least partial coating comprising: (1) at least one starch material comprising at least one hydroxyl group; (2) a second material comprising at least one functional group capable of being reacted with at least one unreacted hydroxyl group of the at least one starch material; (B) breaking a bond between a hydrogen atom of a hydroxyl group of a first starch molecule of the at least one starch material with an oxygen atom of a second starch molecule of the at least one starch material to form at least one unreacted hydroxyl group on the first starch molecule of the at least one starch material; and (C) reacting the at least one functional group of the second material with the at least one unreacted hydroxyl group of the at least one starch material after interweaving.

The present invention further provides a method of forming a resin compatible woven glass fiber fabric, comprising: (A) interweaving a plurality of glass fiber strands to form a fabric, wherein at least one of the plurality of glass fiber strands comprises a plurality of glass fibers and at least one of the plurality of glass fibers comprises an at least partial coating comprising at least one starch material having at least one hydroxyl group; (B) breaking a bond between a hydrogen atom of a hydroxyl group of a first starch molecule of the at least one starch material with an oxygen atom of a second starch molecule of the at least one starch material to form at least one unreacted hydroxyl group on the first starch molecule of the at least one starch material; (C) applying a finishing size to at least a portion of the fabric, the finishing sizing comprising a material comprising at least one functional group capable of being reacted with the at least one unreacted hydroxyl group of the at least one

starch material; and (D) reacting the at least one functional group of the finishing size with at least one at least one hydroxyl group of the at least one starch material.

The foregoing summary, as well as the following detailed description of embodiments of the present invention, will be better understood when read in conjunction with the appended drawings.

Figure 1 is a schematic of a glass fiber forming operation.

Figure 2 is a cross-sectional view of a prepreg incorporating features of the present invention.

Figure 3 is a cross-sectional view of a clad laminate incorporating features of the present invention.

The present invention provides a method of processing glass fibers coated with a starch-oil based sizing system modified to provide for resin compatibility. In particular, fabrics incorporating the starch-oil based sizing can be processed and subsequently can be directly incorporated into matrix materials, and especially into epoxy resin systems for printed circuit boards, without the need for removal of the sizing composition prior to incorporation. Furthermore, the starch-oil sizings subsequently converted into a resin compatible sizing composition are based upon conventional and well known starch-oil sizings compositions and can be readily adapted for use in conventional fiber forming and fabric forming operations, and in particular weaving operations.

For the purposes of this specification, other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

Fig. 1 illustrates a glass fiber forming apparatus 10 according to one nonlimiting embodiment of the present invention. The glass fiber forming apparatus 10 comprises a bushing 12 comprising a plurality of apertures or tips 14 from which streams of molten glass are attenuated by a winder 16 to form a plurality of glass fibers 18. Molten glass 20 can be supplied to the bushing 12, for example, by a forehearth 22 connected directly to a batch glass melting furnace (not shown) or by a pre-melter (not shown) in which marbles or pieces of glass having the desired composition are melted to form the molten glass. Alternatively, the molten glass can be provided to the bushing 12 by melting marbles or pieces of glass having the desired composition in the bushing itself. Such methods of delivering molten glass to a bushing 12 of a fiber forming apparatus 10 are well known in the art. If more information is required, see Loewenstein at pages 85-103 and 117-119, which are hereby incorporated by reference. After the glass fibers 18 are drawn from the bushing 12, they are contacted with an applicator 24 to apply a coating or sizing composition to at least a portion of the surface of the glass fibers 18 to protect the fiber surface from abrasion during forming and provides the necessary handling and processing characteristics. A gathering device 26 mounted at the forming station 10 is used to gather selected groups of fibers 18 and form one or more strands 28 which are wound onto a core 30 at winder 16 to form a package 32. Typically, the fibers 18 are then dried in any convenient manner known in the art. As used herein, the term "strand" means a plurality of individual fibers (the bundle of fibers can also be referred to as "yarn"), and the term "fiber" means an individual filament. The strand can be non-twisted (also referred to as untwisted or zero twist) or twisted prior to incorporation into a fabric, as will be discussed later in more detail.

Fibers useful in the present invention include, but are not limited to, those prepared from fiberizable glass compositions such as "E-glass", "A-glass", "C-glass", "D-glass", "R-glass", "S-glass", and E-glass derivatives. As used herein, the term "fiberizable" means a material capable of being formed into generally continuous fibers, strands or yarns. As used herein, the term "E-glass derivatives" means glass compositions that include minor amounts of fluorine and/or boron and can be fluorine-free and/or boron-free. Furthermore, as used herein "minor amounts of fluorine" means less than 0.5 weight percent fluorine, such as, for example less than 0.1 weight percent fluorine, and "minor amounts of boron" means less than 5 weight percent boron, such as, for example less than 2 weight percent boron. Although not limiting herein, in one particular embodiment of the present invention, glass fibers are formed from E-glass or E-glass derivatives. Such compositions and methods of making glass filaments therefrom are well known to those skilled in the art and

further discussion thereof is not believed to be necessary in view of the present disclosure. If additional information is needed, such glass compositions and fiberization methods are disclosed in Loewenstein at pages 30-44, 47-60, 115-122 and 126-135; and U.S. Patent Nos. 4,542,106 and 5,789,329, which are hereby  
5 incorporated by reference.

Other fiberizable materials that are useful in some nonlimiting embodiments of the present invention include, but are not limited to, fiberizable non-glass inorganic materials, fiberizable organic materials and mixtures and combinations thereof. The inorganic and organic materials can be either man-made or naturally occurring  
10 materials. One skilled in the art will appreciate that the fiberizable inorganic and organic materials can also be polymeric materials. As used herein, the term "polymeric material" means a material formed from macromolecules composed of long chains of atoms that are linked together and that can become entangled in solution or in the solid state<sup>1</sup>. Examples of non-glass inorganic fibers suitable for use  
15 in the present invention include, but are not limited to, ceramic fibers formed from silicon carbide, carbon, graphite, mullite, aluminum oxide, and piezoelectric ceramic materials. Nonlimiting examples of suitable organic fiberizable material include cotton, cellulose, natural rubber, flax, ramie, hemp, sisal, and wool. Nonlimiting examples of suitable polymeric fibers include those formed from polyamides (such as  
20 nylon and aramids), thermoplastic polyesters (such as polyethylene terephthalate and polybutylene terephthalate), acrylics (such as polyacrylonitriles), polyolefins, polyurethanes, and vinyl polymers (such as polyvinyl alcohol). Non-glass fibers believed to be useful in the present invention are discussed at length in the Encyclopedia of Polymer Science and Technology, Vol. 6 (1967) at pages 505-712,  
25 which is hereby incorporated by reference. It is understood that blends or copolymers of any of the above materials and combinations of fibers formed from any of the above materials can be used in the present invention, if desired.

In one nonlimiting embodiment of the present invention, the sizing composition can be a conventional starch-oil sizing of a type well known in the art.  
30 Conventional starch-oil sizings typically comprise at least one starch material; lubricants, such as oils and waxes; softening agents; emulsifiers; anti-static agents; coupling agents, such as silane and titanate coupling agents; and anti-foaming agents. If desired, the sizing can further comprise inorganic fillers, such as boron nitride. Examples of conventional starch-oil sizings that are useful in the present  
35 invention include, but are not limited to, those discussed in Loewenstein (as cited

above) as well as those disclosed in U.S. Patents 4,259,190; 5,210,363; and 5,773,146.

Starch materials useful in the present invention include those starch materials used in conventional starch-oil sizing compositions. Nonlimiting examples of useful starch materials include modified and unmodified starches. Examples of useful modified starches include, but are not limited to, starches modified by acetylation, chlorination, acid hydrolysis, or derivatizing agents, such as phosphatizing, ethoxylating or etherifying agents. Nonlimiting examples of useful unmodified starches include unmodified starches prepared from corn, potatoes, wheat, waxy maize, sago, rice, tapioca, and milo.

While such starch materials are not themselves resin compatible, in one nonlimiting embodiment of the present invention, the sizing composition further comprises a second material comprising at least one functional group capable of being reacted with at least one unreacted hydroxyl group of the starch material to form a grafted starch that is resin compatible. The sizing composition can further comprise an amount of water sufficient to permit the sizing composition to be applied to a surface of a fiber during forming. As used herein, the phrase "capable of being reacted with at least one unreacted hydroxyl group" means that the functional group will react with an unreacted hydroxyl group of the starch material to form a grafted starch material, and the term "grafted starch" means a starch having a hydroxyl group reacted with a functional group. The reaction between an unreacted hydroxyl group of a starch material and a functional group of the second material is accomplished by first breaking the hydrogen bond between starch molecules that form a starch network, i.e. the bond between a hydrogen atom of the hydroxyl group of a first starch molecule with an oxygen atom of a second starch molecule. Breaking the hydrogen bond will break up the starch network and form an unreacted hydroxyl group on the first starch molecule that is exposed to a functional group of the second material. The functional group can then react with the exposed, unreacted hydroxyl group on the first starch so that the hydrogen atom of the hydroxyl group of the first starch cannot rebond to an oxygen atom of the second starch molecules and reform the starch network. It is believed that by reacting the functional group of the second material with a hydroxyl group of the starch material, the tight structure of the starch network can be relaxed or disrupted, thereby permitting the resin matrix material into which the sized fibers is incorporated to penetrate and swell the starch molecules, thereby improving the resin compatibility of

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<sup>1</sup> James Mark et al. Inorganic Polymers, Prentice Hall Polymer Science and Engineering



the sizing composition. Furthermore, it is believed that if the second material comprises oleophilic chain segments or molecules that are compatible with the matrix material into which the coated fibers are incorporated, by associating the oleophilic segments with the starch molecules, i.e. by reacting the functional group of the second material with a hydroxyl group of the starch, the resin compatibility of the sizing can be improved.

Thus one nonlimiting embodiment of the present invention is a sizing composition comprising at least one starch comprising at least one hydroxyl group and at least one second material comprising at least one functional group capable of being reacted with an unreacted hydroxyl group of the at least one starch material. In another nonlimiting embodiment, the sizing composition comprises at least one starch comprising an unreacted hydroxyl group and at least one second material comprising at least one functional group capable of being reacted with the unreacted hydroxyl group of the at least one starch material. In another nonlimiting embodiment, the sizing comprises at least one grafted starch formed by reacting an unreacted hydroxyl group of at least one starch material with a functional group of at least one second material.

The hydrogen bonds in the starch can be broken in any convenient manner known in the art, such as, for example, soaking the coated fibers and/or fabric incorporating the coated fibers in a polar solvent in a manner that will not remove the starch. More specifically, prolonged treatment of the coated fiber, e.g. by soaking them in a solvent, can dissolve or otherwise remove the starch coating from the fiber surface. As is apparent to one skilled in the art, the length of time that the coated fiber and/or fabric should be treated depends, in part, on the type of treatment and the sizing composition. Nonlimiting materials that can be used as such solvents include sodium hydroxide, potassium hydroxide, pyridine, dimethylformamide and N-methylpyrrolidone.

As will be discussed later in more detail, in one nonlimiting embodiment of the present invention, the coated fiber strands are interwoven together to form a woven fabric. It should be appreciated that in a typical fabric weaving operation, warp yarns are coated with a slashing composition prior to weaving, usually a polyvinyl alcohol containing composition, to provide further protection to the warp yarn as the fill yarns are inserted into the warp shed (as will be discussed later in more detail). It is expected that the polar solvent used to break the hydrogen bond between the starch molecules will dissolve the slashing composition so that it will have minimal, if any,

effect on the ability of the solvent to break up the starch network and expose unreacted hydroxyl groups on the starch.

Functional groups that are capable of being reacted with a hydroxyl group of the starch material to form a grafted starch that is resin compatible include, but are not limited to, isocyanate groups; acid groups; acid anhydride groups, vinyl ester groups, acid chloride groups and acrylonitrile groups.

In one nonlimiting embodiment of the present invention, the functional group in the second material is an isocyanate group, and the second material can be selected from, for example, isocyanatosilanes; methyl isocyanate; n-butyl isocyanate; cyclohexyl isocyanate; octadecyl isocyanate; phenyl isocyanate; chlorophenyl isocyanate; isopropyl isocyanate; propyl isocyanate; dichlorophenyl isocyanate; fatty acid ester isocyanates; and aliphatic isocyanates.

In another nonlimiting embodiment of the present invention, the functional group of the second material is an acid group, and the second material can be selected from, for example, formic acid, acetic acid, propionic acid, glutaric acid and butyric acid and high molecular weight acids selected from palmitic acid, lauric acid and stearic acid.

In another nonlimiting embodiment of the present invention, the functional group of the second material is an acid anhydride group, and the second material can be selected from, for example, acetic anhydride, maleic anhydride and succinic anhydride.

In another nonlimiting embodiment of the present invention, the functional group of the second material is a vinyl ester group, and the second material can be selected from, for example, vinyl acetate and vinyl butyrate.

In another nonlimiting embodiment of the present invention, the functional group of the second material is an acid chloride group, and the second material can be selected from, for example, benzoyl chloride and cinnamoyl chloride.

Although not limiting herein, in one embodiment the second material comprises a single functional group that is capable of being reacted with a single hydroxyl group of the starch material, i.e. the second material has only one functional group capable of being reacted with an unreacted hydroxyl group of the starch molecules. Although not meant to be bound by any particular theory, it is believed that if the second material comprises more than one functional group capable of being reacted with multiple unreacted hydroxyl groups of the starch molecule, the starch materials can become networked if the functional groups react with the hydroxyl groups of two or more starch molecules. Such starch networks are not desirable in that they tend to resist swelling and wetting by the matrix materials into

which the coated fibers are incorporated. In other words, highly networked starch molecules can reduce the resin compatibility of the glass fibers sized therewith.

In another nonlimiting embodiment of the present invention, the second material includes multiple functional groups which normally are capable of reacting with the unreacted hydroxyl groups of the starch material, wherein some of the functional groups are blocked or capped (as discussed below in more detail) such that only a selected number of the functional groups, for example one functional group, is capable of being reacted with an unreacted hydroxyl group of the starch material. More particularly and without limiting the present invention, at least one functional group of the second material is blocked or capped to form a blocked or capped functional group. As used herein, the terms "blocked functional group" and "capped functional group" mean that the functional group of the second material is reversibly reacted with a blocking agent to control or reduce the reactivity of the functional group. Although not meant to be bound by any particular theory, it is believed that by incorporating materials comprising blocked functional groups that can be controllably reacted with the hydroxyl groups of starch material in conventional starch-oil type sizing compositions, resin compatible coatings can be formed on the glass fibers and glass fabrics by unblocking the functional group and reacting the unblocked (or free) functional group with unreacted hydroxyl groups of the starch materials, e.g. after forming the fabric, without the need for degreasing the fabric, e.g. heating cleaning the fabric. Thus, conventional technologies that have been developed for fabricating glass fibers and glass fabrics can be used to form the glass fibers and glass fabrics according to the present invention. Then, after forming the glass fibers and glass fabrics, the coated fibers and/or fabric can be processed to break selected hydrogen bonds of the hydroxyl groups in the starch materials and expose unreacted hydroxyl groups, as discussed above, and the blocked functional groups of the sizing can be unblocked and reacted with the unreacted hydroxyl groups, as discussed above, thus preventing the hydrogen bonds from reforming and resulting in a resin compatible coating on at least a portion of the glass fibers and glass fabrics. Although not limiting in the present invention, the blocked functional group(s) can be unblocked by heating and/or chemical reaction. Accordingly, by using the sizing compositions of the present invention, resin compatible glass fabrics can be formed without degradation of the glass fibers caused by conventional degreasing operations, e.g. the high temperatures associated with heat cleaning processes. In one nonlimiting embodiment of the present invention, the second material is BAYBOND 116 water-reducible blocked polyisocyanate commercially available from Bayer Corporation, Pittsburgh, PA.

It will be appreciated by those skilled in the art that in an embodiment of the present invention wherein heat is used to unblock the functional group, the temperature at which a blocked functional group will become unblocked will depend, in part, on the blocking agent and/or catalysts (discussed below) used in the sizing composition. However, this temperature will generally be significantly lower than that used in typical heat cleaning processes. Similarly, the type of chemical reaction required to unblock a blocked functional group will also depend, in part, on the blocking agent and/or the catalyst used in the sizing composition.

Although not required, in another nonlimiting embodiment of the present invention, the grafted starch material is essentially free of unreacted or blocked functional groups. As used herein, the phrase "essentially free of unreacted or blocked functional groups" means that the grafted starch material comprises no greater than 5 percent of unreacted or blocked functional groups based on the total number of functional groups associated with the grafted starch material, such as, for example no greater than 1 percent of unreacted or blocked functional groups based on the total number of functional groups associated with the grafted starch material. Although not limiting herein, in one embodiment the grafted starch is free of unreacted or blocked functional groups, i.e. the grafted starch comprises no functional group that have not been reacted with a hydroxyl group of the starch.

In one nonlimiting embodiment of the present invention, the blocked functional groups in the sizing composition are blocked isocyanate groups. Blocking agents suitable for use with the isocyanate groups of this particular embodiment include, but are not limited to, secondary and tertiary alcohols; active methylene compounds; oximes; lactams; phenols; and heterocyclic hydroxyl compounds.

For example and although not limiting herein, if the functional group is an isocyanate group, the isocyanate group can be initially reacted with a phenol blocking agent to form a phenylurethane which can render the isocyanate group relatively unreactive with the hydroxyl groups of the starch and/or the water of the sizing composition. Thus, the sizing composition can be applied to the glass fibers in a conventional manner and the glass fibers can be processed into glass fiber fabrics using conventional techniques. After forming the glass fiber fabric, the fabric can be processed to break the hydrogen blocks and expose the hydroxyl groups, e.g. soaking the fabric in a solvent. The fabric can then be heated, e.g. to 150°C (302°F), to unblock the isocyanate group from the phenol blocking agent so that an unblocked (or free) isocyanate group can be reacted with an unreacted hydroxyl group of the starch material to form a resin compatible, carbamate grafted starch. See Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 12 (2<sup>nd</sup> Ed., 1967) at pages 45-

53, which are hereby incorporated by reference. Although not required, the fabric can be further heated to volatilize the blocking agent liberated when the isocyanate is unblocked. If desired, the fabric can be further treated with a conventional finishing size before incorporation into the matrix material or it can be directly incorporated into the matrix material without being treated with a finishing size.

Although not required, if desired, the sizing compositions of the present invention can further comprise a catalyst material capable of catalyzing the reaction between an unreacted hydroxyl group of the starch material and a functional group of the second material. Examples of suitable catalyst for use with isocyanate functional groups include, but are not limited to, pyridine and tertiary amines.

A nonlimiting aspect of the present invention is a glass fiber strand 28 comprising a plurality of glass fibers 18, at least one of the plurality of glass fibers 18 comprising an at least partial coating comprising at least one starch material comprising at least one hydroxyl group and at least one second material comprising at least one functional group capable of being reacted with an unreacted hydroxyl group of the at least one starch material. In another nonlimiting embodiment, glass fiber strand 28 comprises a plurality of glass fibers 18, at least one of the plurality of glass fibers 18 comprising an at least partial coating comprising at least one starch material comprising at least one unreacted hydroxyl group and at least one second material comprising at least one functional group capable of being reacted with the at least one unreacted hydroxyl group. In another nonlimiting embodiment, glass fiber strand 28 comprises a plurality of glass fibers 18, at least one of the plurality of glass fibers 18 comprising an at least partial coating comprising at least one grafted starch formed by reacting an unreacted hydroxyl group of a starch material with a functional group of a second material.

In another nonlimiting embodiment of the present invention, a glass fiber strand 28 comprises a plurality of glass fibers 18, wherein at least one of the plurality of glass fibers 18 comprises an at least partial coating comprising at least one carbamate grafted starch material. Although not limiting herein, the carbamate grafted starch material can be a reaction product of at least one starch material comprising at least one unreacted hydroxyl group and at least one second material comprising at least one isocyanate group capable of reacting with at least one unreacted hydroxyl group of the at least one starch material. As previously discussed and although not limiting herein, it is believed that by reacting the isocyanate group of the second material with unreacted hydroxyl group of the starch material, for example after forming the fabric, a resin compatible coating comprising a carbamate grafted starch material can be formed on the glass fabric after forming the

glass fiber fabric without the need for fabric degreasing, and in particular without the need for heat cleaning operations.

It should be appreciated that in one particular nonlimiting embodiment of the invention, the partial coating is at least the partial residue of an aqueous sizing  
5 composition comprising starch materials and second materials as discussed herein.

In another nonlimiting aspect of the present invention, a fiber strand comprises a plurality of fibers, wherein at least one of the plurality of fibers comprising an at least partial coating comprises a carbamate grafted starch that is essentially free of unreacted or blocked isocyanate groups.

10 As discussed above, the coated fiber strands discussed above can be processed into fabric, such as wovens, nonwovens (including, but not limited to, unidirectional, biaxial and triaxial fabrics), knits, mats (both chopped and continuous strand mats) and multilayered fabrics (i.e. overlaying layers of fabric held together by stitching or some other material to form a three-dimensional fabric structure). In  
15 addition, the coated fiber strands used as warp and weft (i.e. fill) strands of a fabric can be non-twisted (also referred to as untwisted or zero twist) or twisted prior to forming the fabric and the fabric can include, but is not limited to, various combinations of both twisted and non-twisted warp and weft strands. The fabrics can also be formed into other types of fiber products such as, e.g. chopped strand or  
20 roving.

As a result, another nonlimiting embodiment of the present invention includes a fabric comprising at least one glass fiber strand comprising a plurality of glass fibers, at least one of the plurality of glass fibers comprising an at least partial coating comprising at least one starch material comprising at least one hydroxyl group  
25 reacted with at least one functional group of a second material after the fabric is formed. Although not limiting in the present invention, the reacted starch can comprise at least one carbamate grafted starch material. Although not required, the carbamate grafted starch material can be a reaction product of at least one starch material comprising at least one unreacted hydroxyl group and a second material  
30 comprising at least one isocyanate group capable of being reacted with the at least one unreacted hydroxyl group of the at least one starch material.

Although not limiting in the present invention, in one embodiment, a resin compatible fabric of the present invention can be formed from yarn coated with a conventional starch-oil sizing, e.g. 695 sizing which is a starch-oil sizing available  
35 from PPG Industries, Inc. of Pittsburgh, PA, and soaked in an aqueous solution of sodium hydroxide having a pH ranging from 9 to 11 for one hour at room temperature (22°C). This basic condition of the sodium hydroxide solution makes the solvent

more polar and promotes the breakage of the hydrogen bonds in the starch. The fabric is then soaked at room temperature in an aqueous solution comprising an anhydride, such as acetic anhydride, with the solution kept at a pH ranging from 9 to 11 by adding sodium hydroxide, so that the acid anhydride functional groups can  
5 react with the exposed unreacted hydroxyl groups and make the coating more resin compatible. The acetic anhydride solution is kept between 9 and 11 to prevent the hydrogen bonds from reforming and promote the preferential reaction of the functional groups on the acetic anhydride with the exposed OH groups. The fabric can then be neutralized with dilute hydrochloric acid and then washed with water and  
10 dried. It is estimated that 8 g of acetic anhydride can treat 1000 g of starch based fabric based on an LOI of 1% and a sizing composition that is 50% starch based on solids weight, and the resulting fabric will have a degree of substitution of 0.5 as compared to a theoretical degree of substitution of 3. As used herein, the "theoretical degree of substitution" is the number of OH groups on each starch repeat unit that  
15 can be reacted.

In another nonlimiting embodiment of the present invention, a resin compatible fabric can be formed from yarn coated with a conventional starch-oil sizing, and soaked in a refluxing pyridine solution for one hour. The fabric is then soaked in pyridine solution comprising an anhydride, such as acetic anhydride, at  
20 100°C (212°F) for another hour so that the acid anhydride functional groups can react with the exposed unreacted hydroxyl groups and make the coating more resin compatible. The fabric can then be washed with ethanol and dried. It is estimated that 13 g of acetic anhydride can treat 1000 g of starch based fabric based on an LOI of 1% and a sizing composition that is 50% starch based on solids weight, and the  
25 resulting fabric will have a degree of substitution of 3.

In another nonlimiting embodiment of the present invention, a resin compatible fabric can be formed from yarn coated with a conventional starch-oil sizing and soaked in an aqueous solution of sodium hydroxide having a pH ranging from 9.5 to 11 for 1 hour at 100°C (212°F). The fabric is then soaked in an aqueous  
30 solution comprising a vinyl ester, such as vinyl acetate, for 1 hour at 100°C (212°F), with the solution kept at a pH ranging from 9.5 to 11 by adding sodium hydroxide, so that the vinyl ester functional groups can react with the exposed unreacted hydroxyl groups and make the coating more resin compatible. The fabric can then be neutralized with dilute hydrochloric acid and then washed with water and dried. It is  
35 estimated that 0.5 g of vinyl acetate can treat 1000 g of starch based fabric based on an LOI of 1% and a sizing composition that is 50% starch based on solids weight,

and the resulting fabric should have a degree of substitution of 2.2 as compared to a theoretical degree of substitution of 3.

In another nonlimiting embodiment of the present invention, a resin compatible fabric can be formed from yarn coated with a conventional starch-oil sizing by (i) soaking the fabric in a pyridine for 1 hour at 100°C (212°F), (ii) removing any moisture from the fabric, e.g. heating and drying the fabric, and (iii) soaking the fabric in a 5% solution of hexamethylene diisocyanate or phenol isocyanate in pyridine for 1 hour at 100°C (212°F) so that the functional groups can react with the exposed, unreacted hydroxyl groups of the starch and make the coating more resin compatible. The fabric can then be washed with ethanol and dried. It is estimated that 20 g of phenol isocyanate can treat 1000 g of starch based fabric based on an LOI of 1% and a sizing composition that is 50% starch based on solids weight, and the resulting fabric will have a degree of substitution of 3.

In one nonlimiting embodiment of the present invention, the second material of the sizing composition is applied to the fibers and/or fabric after an initial coating is applied, e.g. as a finishing size. More particularly and without limiting the present invention, a conventional starch-oil sizing composition comprising at least one starch material comprising at least one hydroxyl group can be applied to glass fibers during forming and the glass fibers can be subsequently formed into a glass fabric. Thereafter, the fabric can be treated to break the hydrogen bonds and expose at least one unreacted hydroxyl group. A finishing sizing comprising a second material comprising at least one functional group capable of being reacted with an unreacted hydroxyl group of the at least one starch material of the conventional starch-oil sizing can be applied to the fabric and the at least one functional group can then be reacted with at least one hydroxyl group to form a resin compatible coating composition, as discussed above.

In one nonlimiting embodiment of the present invention, the second material is a finishing size comprising hydrolyzable silanes having at least one functional group reactable with an unreacted hydroxyl group. A specific, nonlimiting example of a silane comprising a functional group that will react with an unreacted hydroxyl group of the starch material of the present invention is A1310 silane, which includes an isocyanate functional group and is commercially available from Crompton Corporation of Greenwich, CT.

In still another nonlimiting embodiment of a finishing size according to the present invention, the functional group is an isocyanate group that is reacted with an unreacted hydroxyl group of the starch material to form a carbamate grafted starch material that is resin compatible.



In another nonlimiting embodiment of the present invention, fabrics made in accordance with the present invention comprise an at least partial coating comprising a grafted starch that is essentially free of unreacted or blocked isocyanate groups.

Nonlimiting methods of forming glass fibers, strands, yarns, and fabrics  
5 according to the present invention will now be discussed generally.

In another nonlimiting embodiment of the present invention, a resin compatible fabric incorporating a plurality of glass fiber strands is formed, wherein at least one of the glass fibers of the glass fiber strands comprises an at least partial coating comprising at least one starch material comprising at least  
10 one hydroxyl group and a second material comprising at least one functional group capable of being reacted with at least one exposed unreacted hydroxyl group of the at least one starch material. The method further comprises breaking a bond between a hydrogen atom of a hydroxyl group of a first starch molecule with an oxygen atom of a second starch molecule to form at least one  
15 unreacted hydroxyl group on the first starch molecule; and reacting the at least one functional group with the at least one unreacted hydroxyl group of the at least one starch material after forming the fabric. Although not limiting herein, in one nonlimiting embodiment the functional group is an isocyanate group which is blocked with a blocking agent and the reacting step includes heating the fabric to  
20 unblock the at least one blocked isocyanate group. Although not required, if desired, the blocking agent can be decomposed after unblocking by, for example, heating the fabric to a temperature suitable for decomposing or volatilizing the blocking agent.

In another nonlimiting embodiment of the present invention, a fabric is formed from a plurality of fiber strands, wherein at least one of the plurality of fiber strands  
25 comprises at least one fiber at least partially coated with a coating composition comprising at least one starch material having at least one hydroxyl group. After forming the fabric, a finishing size comprising at least one second material comprising at least one functional group capable of being reacted with at least one unreacted hydroxyl group of the at least one starch material is applied to at least a  
30 portion of the fabric. Either before or after applying the finishing size, the fabric is processed to break selected hydrogen bonds forming the starch network and expose at least one unreacted hydroxyl group of the starch material. Thereafter, the functional group of the at least one second material is reacted with the at least one exposed hydroxyl group of the at least one starch material. In one non-limiting  
35 embodiment, the second material comprises a silan and the functional group is an isocyanate group. The resulting grafted starch is a carbamate grafted starch.

Furthermore, although not required, the finishing size can further comprise an amount of water sufficient to permit the finishing size to be uniformly coated on to the fabric. In one nonlimiting embodiment of the invention wherein the finishing size comprises water, the functional group is blocked with a blocking agent as previously discussed that also prevents any undesired reactions between the functional group and the water.

In one nonlimiting embodiment of the fabric of the present invention, the fabric is a woven fabric. Fabric weaving is accomplished by interweaving first and second glass fiber strands, and in particular warp and fill yarn, on a loom in a manner well known in the art. Although not limiting herein, the fabric can be woven using an air jet loom, which is a type of loom wherein the weft (or fill) yarn is inserted into a warp shed formed by the warp yarn by a blast of compressed air. Nonlimiting examples of commercially available air jet looms include Model Nos. 103, 103I 1033 or ZAX looms available from Tsudakoma of Japan and Model Nos. L-5000, L-5100 or L-5200 looms available from Sulzer Brothers LTD. of Zurich, Switzerland.

The present invention further contemplates preregs, laminates, and electronic supports formed from the aforementioned glass fabrics made in accordance with the present invention. As used herein, the term "prepreg" means a fabric that is at least partially impregnated with a matrix material which has been at least partially cured; the term "laminate" means a multilayered structure that includes at least one fabric layer; and the term "electronic support" means a structure that mechanically supports and/or electrically interconnects elements such as, but not limited to, active electronic components, passive electronic components, printed circuits, integrated circuits, semiconductor devices and other hardware associated with such elements including, but not limited to, connectors, sockets, retaining clips and heat sinks.

Referring now to Fig. 2, there is shown a prepreg 240 comprising a fabric 242 comprising an at least partial coating 244 comprising a grafted starch material as discussed herein and a matrix material 246 applied to at least a portion of the fabric 242. In one nonlimiting embodiment, the starch material comprises a carbamate grafted starch material.

Although not limiting herein, matrix materials 246 useful in forming the preregs 240 of the present invention include, but are not limited to, thermosetting polymeric materials such as thermosetting polyesters, vinyl esters, epoxides (containing at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols), phenolics, aminoplasts, thermosetting polyurethanes, and derivatives and mixtures thereof. Suitable matrix materials for

forming laminates for printed circuit boards include, but are not limited to, FR-4 epoxy resins, which are polyfunctional epoxy resins such as difunctional brominated epoxy resins, polyimides and liquid crystalline polymers, the compositions of which are well known to those skilled in the art. If further information regarding such compositions is needed, see Electronic Materials Handbook<sup>TM</sup>, ASM International (1989) at pages 534-537, which are specifically incorporated by reference herein.

Nonlimiting examples of suitable thermoplastic matrix materials include polyolefins, polyamides, thermoplastic polyurethanes, thermoplastic polyesters, vinyl polymers, and mixtures thereof. Further examples of useful thermoplastic materials include polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polyvinyl chlorides, and polycarbonates.

A specific, nonlimiting example of a matrix material formulation useful in the present invention consists of EPON 1123-A80 epoxy resin (commercially available from Shell Chemical Company of Houston, Texas), dicyandiamide, 2-methylimidazole, and DOWANOL PM glycol ether (commercially available from The Dow Chemical Co. of Midland, Michigan).

Other components which can be included in prepreg layer 240 include, but are not limited to, colorants or pigments, lubricants or other processing aids, ultraviolet light (UV) stabilizers, antioxidants, flame retardants and other fillers and extenders.

In another nonlimiting embodiment of the present invention, two or more prepregs 340 are stacked together and laminated to form a laminate 350 as shown in Fig. 3, wherein at least one of the prepregs incorporates resin compatibilized fabrics as discussed herein. Most typically, although not limiting in the instant invention, the prepreg is cut (or punched) to a required size and two or more cut prepreg layers are stacked together, laminated, and cured by pressing the stack, e.g. between polished steel plates, at elevated temperatures and pressures for a predetermined length of time, to cure the matrix material and form laminate 350 of a desired thickness.

Although not required, if desired, a layer 352 of an electrically conductive material can be positioned on and secured to at least a portion of at least one surface 354 of the laminate 350. For example, although not limiting herein, a metal foil can be laminated together with at least one prepreg layer 340 by positioning the foil 352 on surface 354 of the at least one of the prepreg layer 340 prior to laminating.

Thereafter, the stack can be laminated to form a clad laminate. As used herein the term "clad laminate" means a laminate 350 having an electrically conductive material 352 on at least a portion of one or more surfaces 354 thereof.

In one nonlimiting embodiment of the present invention, one or more circuits are patterned in the electrically conductive material of the clad laminate to form a printed circuit board. As used herein, the term "printed circuit board" (PCB) (sometimes referred to as an "electronic circuit board" or "printed wiring board") means an electronic support which can be reinforced with a reinforcement material, and comprising one or more printed circuits and/or aperture(s). The term "circuit(s)" means any feature formed in, or by, an electrically conductive material and includes, for example, but not limiting herein, lines, pads, lands and other features normally formed on printed circuit boards in order to provide the necessary electrical and/or thermal interconnections.

It will be recognized by those skilled in the art that the prepregs, laminates and clad laminates of the present invention can be useful in forming multilayer printed circuit boards that are well known in the art. As used herein the term "multilayer printed circuit board" means a printed circuit board having at least one internal layer of an electrically conductive material. The internal layer can be present as an essentially continuous plane (i.e. a power or ground plane) or it can be patterned with one or more circuits as discussed below.

Methods of forming prepregs, laminates, and printed circuit boards according to the present invention will now be discussed generally.

A method of forming a prepreg according to the present invention comprises obtaining a resin compatible glass fabric comprising at least one fiber comprising an at least partial coating comprising a grafted starch material formed as discussed herein. A matrix material is applied to at least a portion of the fabric and is at least partially cured to form a prepreg. Although not limiting herein, the matrix material can be an epoxy material that is applied by submerging the fabric in a bath comprising the epoxy material and a solvent. After submerging the fabric in the bath, the fabric is passed between a pair of metering rolls and subsequently B-staged (i.e. at least partially dried or cured), e.g. by passing the epoxy impregnated fabric through a drier. Although not limiting herein, in one nonlimiting embodiment the fabric is a non-degreased fabric, e.g. a fabric that is not subjected to coating removal, e.g. heat cleaning and/or scrubbing. Although not limiting herein, in one embodiment the grafted starch material comprises at least one carbamate grafted starch material which, although not required, can be the reaction product of at least one starch material comprising at least one unreacted hydroxyl group and a second material comprising an isocyanate group capable of being reacted with at least one hydroxyl group of the at least one starch material.

A method of forming a laminate according to the present invention comprises obtaining at least one prepreg comprising a resin compatible fabric comprising at least one fiber comprising an at least partial coating comprising a grafted starch material formed as disclosed herein, stacking it with at least one additional layer, e.g.  
5 another prepreg and/or an electroconductive layer. The stack of material is then subjected to elevated temperature and pressure for a predetermined period of time to form a laminate as discussed above. Although not limiting herein, in one embodiment the grafted starch material comprises at least one carbamate grafted  
10 starch material which, although not required, can be the reaction product of at least one starch material comprising at least one unreacted hydroxyl groups and a second material comprising an isocyanate group capable of being reacted with the at least one unreacted hydroxyl group of the at least one starch material. In another nonlimiting embodiment of the invention, the fabric can be a non-degreased fabric.

A method of forming a printed circuit board according to the present invention  
15 will now be discussed generally. The method comprises obtaining a laminate comprising a glass fiber fabric comprising at least one fiber comprising an at least partial coating comprising a grafted starch material formed as disclosed herein. After obtaining the laminate, a circuit is patterned onto at least a portion of the laminate by, for example, depositing an electrically conductive material onto the laminate to form  
20 the circuit or by etching a portion of an electrically conductive material positioned on a surface of the laminate (i.e. the laminate is a clad laminate). Although not limiting herein, in one embodiment the grafted starch material comprises at least one carbamate grafted starch material which, although not required, can be the reaction product of at least one starch material comprising at least one unreacted hydroxyl  
25 groups and a second material comprising an isocyanate group capable of being reacted with the at least one unreacted hydroxyl group of the at least one starch material. In another nonlimiting embodiment of the invention, the fabric can be a non-degreased fabric.

It will be appreciated by those skilled in the art that changes could be made to  
30 the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications that are within the spirit and scope of the invention, as defined by the appended claims.

## WE CLAIM:

1. A method a forming a resin compatible fabric comprising:

(A) forming a fabric comprising a plurality of fiber strands, wherein  
5 at least one of the plurality of fiber strands comprises a plurality of fibers and  
at least one of the plurality of fibers comprises an at least partial coating  
comprising at least one starch material comprising at least one hydroxyl  
group;

(B) breaking a bond between a hydrogen atom of a hydroxyl group  
10 of a first starch molecule of the at least one starch material with an oxygen  
atom of a second starch molecule of the at least one starch material to form  
at least one unreacted hydroxyl group on the first starch molecule; and

(C) reacting at least one functional group of a second material with  
the at least one unreacted hydroxyl group of the at least one starch material  
15 to form a grafted starch material after forming the fabric.

2. The method according to claim 1, wherein forming comprises  
interweaving the plurality of fiber strands to form a woven fabric.

3. The method according to claim 1, wherein the coating further  
20 comprises the second material comprising the at least one functional group capable  
of being reacted with the at least one unreacted hydroxyl group of the at least one  
starch material.

4. The method according to claim 1, further comprising applying a  
25 finishing size to a least a portion of the fabric, the finishing sizing comprising the  
second material comprising the at least one functional group capable of being  
reacted with the at least one unreacted hydroxyl group of the at least one starch  
material.

5. The method according to claim 1, wherein at least one of the plurality  
30 of fiber strands comprises glass fibers selected from E-glass fibers, D-glass fibers, S-  
glass fibers, Q-glass fibers, A-glass fibers and E-glass derivative fibers.

6. The method according to claim 1, wherein the at least one starch  
35 material is selected from modified and unmodified starches.

7. The method according to claim 1, wherein the second material is a silane.

8. The method according to claim 7, wherein the silane is an isocyanatosilane.

9. The method according to claim 1, wherein the at least one functional group is selected from isocyanate groups, acid anhydride groups, acid groups, vinyl ester groups, acid chloride groups and acrylonitrile groups.

10

10. The method according to claim 9, wherein the at least one functional group is selected from an isocyanate group, and the second material is selected from isocyanatosilanes, methyl isocyanate, n-butyl isocyanate, cyclohexyl isocyanate, octadecyl isocyanate, phenyl isocyanate, chlorophenyl isocyanate, isopropyl isocyanate, propyl isocyanate, dichlorophenyl isocyanate, fatty acid ester isocyanates, and aliphatic isocyanates.

15

11. The method according to claim 10, wherein at least one isocyanate group is blocked with a blocking agent, and further comprising unblocking the at least one blocked isocyanate group and reacting the unblocked isocyanate group with the at least one unreacted hydroxyl group of the starch material.

20

12. The method according to claim 11, wherein the blocking agent is selected from secondary and tertiary alcohols, active methylene compounds, oximes, lactams, phenols, and heterocyclic hydroxyl compounds.

25

13. The method according to claim 12, wherein at least one functional group is at least one isocyanate group initially reacted with a phenol blocking agent, further comprising heating the fabric to unblock the at least one isocyanate group so that the unblocked isocyanate group can react with the unreacted hydroxyl group of the at least one starch material.

30

14. The method according to claim 9, wherein the second material comprises at least one isocyanate group which reacts with the at least one unreacted hydroxyl group of the at least one starch material to form a carbamate grafted starch material.

35

15. The method according to claim 14, wherein the carbamate grafted starch material is essentially free of unreacted or blocked isocyanate groups.

16. The method according to claim 9, wherein the at least one functional group is selected from an acid anhydride group, and the second material is selected from acetic anhydride, maleic anhydride and succinic anhydride.

17. The method according to claim 9, wherein the at least one functional group is selected from an acid group, and the second material is selected from formic acid, acetic acid, propionic acid, glutaric acid and butyric acid and high molecular weight acids selected from palmitic acid, lauric acid and stearic acid.

18. The method according to claim 9, wherein the at least one functional group is selected from a vinyl ester group, and the second material is selected from vinyl acetate and vinyl butyrate.

19. The method according to claim 9, wherein the at least one functional group is selected from an acid chloride group, and the second material is selected from benzoyl chloride and cinnamoyl chloride.

20. The method according to claim 1, wherein at least a portion of the fiber strand is twisted.

21. The method according to claim 1 wherein the coating further comprises at least one catalyst material capable of catalyzing the reaction between at least one unreacted hydroxyl group of the at least one starch material and the at least one functional group of the second material.

22. The method according to claim 21, wherein the catalyst material is selected from pyridine and tertiary amines.

23. The method according to claim 1, wherein the coating is essentially free of blocked functional groups.

24. The method according to claim 1 comprising at least one inorganic filler material.



25. The method according to claim 24, wherein the at least one inorganic filler material is boron nitride.

26. The method according to claim 1, wherein breaking comprises  
5 soaking the fabric in a polar solvent.

27. The method according to claim 26, wherein the polar solvent is selected from sodium hydroxide, potassium hydroxide, pyridine, dimethylformamide, and N-methylpyrrolidone.  
10

28. The method according to claim 1, wherein breaking comprises soaking the fabric in an aqueous solution of sodium hydroxide having a pH ranging from 9 to 11, and reacting comprises soaking the fabric in an aqueous solution  
15 comprising an anhydride, while maintaining the solution at a pH ranging from 9 to 11.

29. The method according to claim 1, wherein breaking comprises soaking the fabric in a refluxing pyridine solution, and reacting comprises soaking the fabric in pyridine solution comprising an acid anhydride.  
20

30. The method according to claim 1, wherein breaking comprises soaking the fabric in an aqueous solution of sodium hydroxide having a pH ranging from 9.5 to 11, and reacting comprises soaking the fabric in an aqueous solution comprising a vinyl ester, while maintaining the solution at a pH ranging from 9.5 to  
25 11.

31. The method according to claim 1, wherein breaking comprises soaking the fabric in a pyridine, and reacting comprises soaking the fabric in a 5 % solution of hexamethylene diisocyanate or phenol isocyanate in pyridine  
30

32. A method a forming a resin compatible woven glass fiber fabric, comprising:

(A) interweaving a plurality of glass fiber strands to form a fabric, wherein at least one of the plurality of glass fiber strands comprises a plurality  
35 of glass fibers and at least one of the plurality of glass fibers comprises an at least partial coating comprising:

(1) at least one starch material comprising at least one hydroxyl group;

(2) a second material comprising at least one functional group capable of being reacted with at least one unreacted hydroxyl group of the at least one starch material;

(B) breaking a bond between a hydrogen atom of a hydroxyl group of a first starch molecule of the at least one starch material with an oxygen atom of a second starch molecule of the at least one starch material to form at least one unreacted hydroxyl group on the first starch molecule of the at least one starch material; and

(C) reacting the at least one functional group of the second material with the at least one unreacted hydroxyl group of the at least one starch material after interweaving.

33. A method of forming a resin compatible woven glass fiber fabric, comprising:

(A) interweaving a plurality of glass fiber strands to form a fabric, wherein at least one of the plurality of glass fiber strands comprises a plurality of glass fibers and at least one of the plurality of glass fibers comprises an at least partial coating comprising at least one starch material having at least one hydroxyl group;

(B) breaking a bond between a hydrogen atom of a hydroxyl group of a first starch molecule of the at least one starch material with an oxygen atom of a second starch molecule of the at least one starch material to form at least one unreacted hydroxyl group on the first starch molecule of the at least one starch material;

(C) applying a finishing size to a least a portion of the fabric, the finishing sizing comprising a material comprising at least one functional group capable of being reacted with the at least one unreacted hydroxyl group of the at least one starch material; and

(D) reacting the at least one functional group of the finishing size with at least one at least one hydroxyl group of the at least one starch material.

34. The method according to claim 33, wherein the finishing size is applied after breaking the bond between the hydrogen and oxygen atoms.

35. The method according to claim 33, wherein the material comprises a silane.

36. A prepreg comprising:

- (A) a resin compatible fabric made according to claim 1; and
- (B) a matrix material applied to at least a portion of the fabric.

37. A laminate comprising:

(A) at least one prepreg layer comprising:

- (1) a resin compatible fabric made according to claim 1;

and

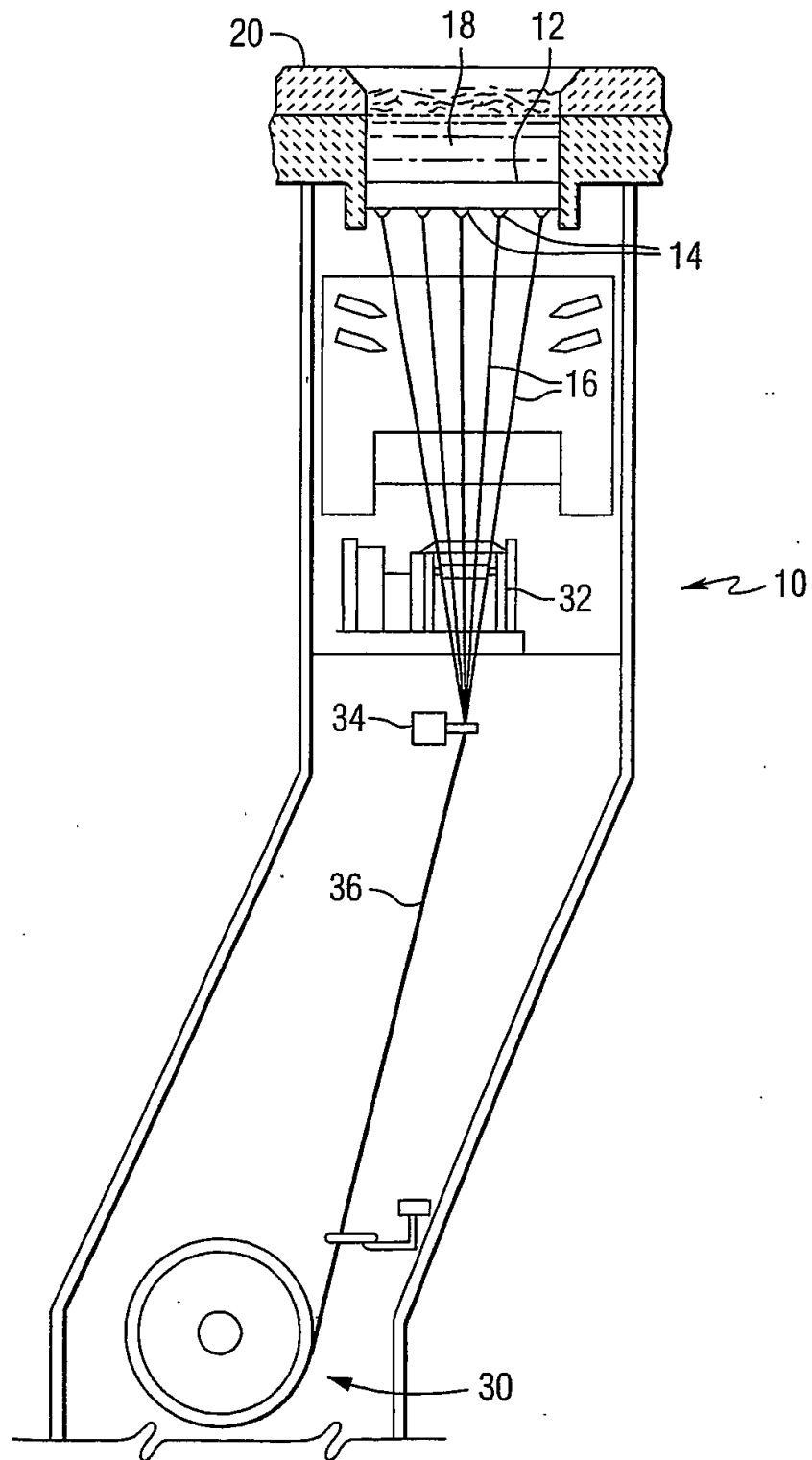
- (2) a matrix material applied to at least a portion of the fabric; and

(B) at least one additional layer laminated to at least a portion of at least one major surface of the at least one prepreg layer.

38. The laminate according to claim 37, wherein the at least one additional layer comprises at least one electrically conductive material.

39. A printed circuit board comprising:

- (A) a resin compatible fabric made according to claim 1;
- (B) a matrix material applied to at least a portion of the fabric; and
- (C) at least one electrically conductive material comprising at least one circuit positioned on at least a portion of at least one surface of the printed circuit board.



**FIG. 1**

2/2

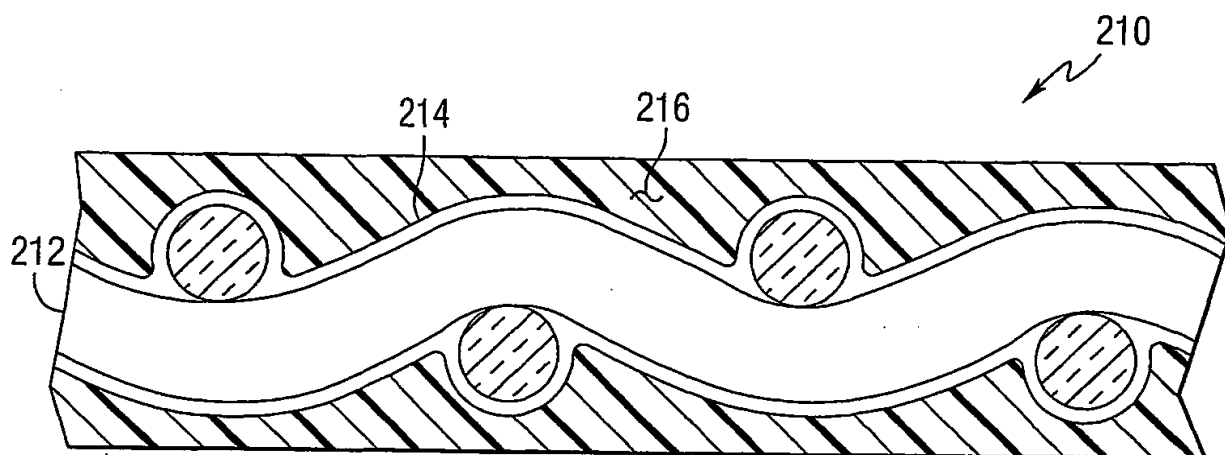


FIG. 2

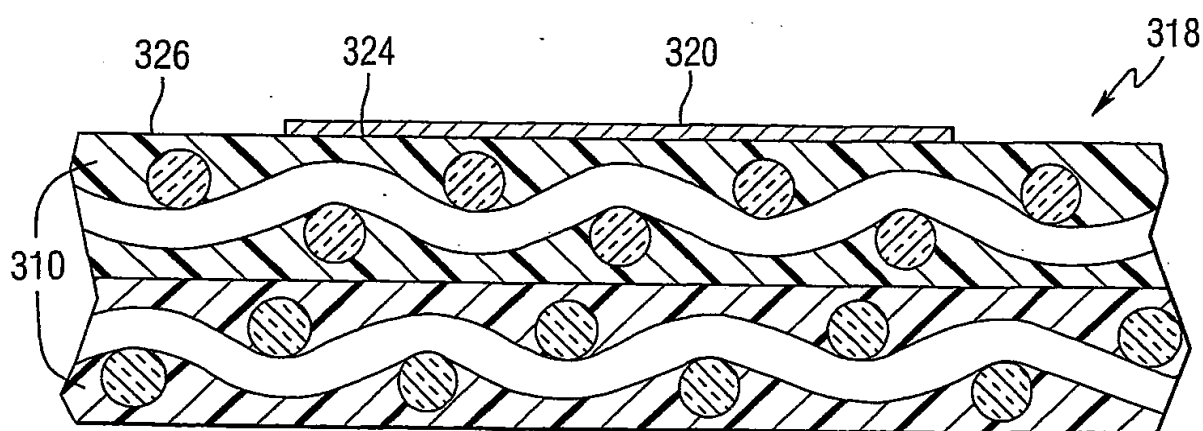


FIG. 3



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/29005

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) :B32B 17/02, 17/04, 27/04, 27/12

US CL :442/180, 181; 428/297.4, 299.4, 901

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 442/180, 181; 428/297.4, 299.4, 901

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,908,689 A (DANA et al) 01 June 1999, see entire document.	1-39
A	US 5,091,465 A (DANA et al) 25 February 1992, see entire document.	1-39

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"Z"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

03 DECEMBER 2001

Date of mailing of the international search report

31 DEC 2001

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